

2 2 1 1 THE COMPOSITION OF TIGHT HAIR SPOTS*

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ABSTRACT

The occurrence of tight hair spots is an indication that the liming process does not proceed uniformly over the entire area of a hide. The spots most resistant to unhairing will thus determine the time required for complete hair removal. Tight hair spots and adjacent normal areas were analyzed for moisture, fat, and ash and calcium, sodium, and chloride ions. Differences in the analytical values for these constituents indicate that the lack of unhairing action is due to delayed penetration of the lime. Possible causes are discussed.



INTRODUCTION

There are a number of systems which have been proposed and used for the unhairing of cattlehides. The time required for each system is the time necessary to obtain practically complete hair removal from all of the hides treated. If a shorter time is used, spots of tight hair remain, indicating that all regions of a hide do not unhair with equal ease. Thus, there is something in the nature of the tight hair spots which dictates the time required for complete hair removal.

A comparison of the composition of tight hair spots with adjacent, completely unhaird areas from the same hide was made to determine what differences existed. Each tight hair spot represents some partial degree of completion of the unhairing reaction. Therefore, comparisons between the various sets of analytical data should indicate the changes occurring during different stages of the unhairing process.

EXPERIMENTAL

Observations made in a commercial tannery on 145 cattlehides which had received less than optimum liming treatment indicated that 17, or about 12%, of the hides had tight hair spots. Immediately after the hides came from the un-

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hairing machines, the location and size of the tight hair spots were indicated on an outline of a hide. These observations were put into a composite picture which illustrates the areas where most of the tight hair spots occur. Samples for analysis were taken from both the tight hair spots and adjacent unhaired areas of some of these hides.

The analytical data on the commercially limed hides indicated some significant trends. These were confirmed in a more controlled unhairing experiment performed in the laboratory. For this laboratory study, a comparison was made between a commercial green-salted hide, a completely limed hide, and a hide containing a tight hair spot. Analyses were performed on both the tight hair spot and a nearby unhaired area.

Commercially limed hides.—These hides were from a regular tannery production run. The green-salted hides were soaked for two days and then fleshed. About 100 hides were put into a vat containing 3,000 gallons of water, 400 lb. of lime, and 50 lb. of sodium sulfide. After 2.5 hours an additional 450 lb. of lime were added. After one day an additional 150 lb. of lime and 50 lb. of sodium sulfide were added, and the hides were allowed to remain in the lime for one more day.

Laboratory-limed hides.—Commercial green-salted hides were soaked overnight, then limed for 7 days at a 5-to-1 float in a mixture of 10% lime and 0.6% sodium sulfide on the green-salted weight. These hides were fleshed after unhairing.

Samples for analysis.—The hair was pulled or shaved from the tight hair spots before sampling to make these samples comparable to the unhaired pieces. Thus, lime slurry trapped by the hair was prevented from influencing the calcium and ash values. The sample pieces were blotted on clean cotton towels to remove surface moisture, and samples for analysis were cut from the desired areas with a one-inch-square die. Duplicate samples were taken, and the results were averaged.

Moisture analysis.—The one-inch-square samples of hides were placed in weighing bottles, weighed, then dried in a vacuum oven at 50°C., using a slow stream of dry air to sweep the liberated moisture from the oven. The samples were weighed daily until a constant dry weight was achieved. The moisture analysis was performed in duplicate, the percentage of dry material was calculated, and all subsequent tests were reported on a moisture-free basis.

Ash analysis.—The samples of hides were ashed slowly in a muffle furnace by ALCA Standard Method B-15 (1). The temperature was raised gradually over 1½ hours to 600°C. This temperature was maintained for at least 2 hours and, if necessary, for additional time until the ash was white.

Preparation of solutions of the ash for analysis.—Some of the ash samples were dissolved in 1 ml. of acetic acid and made up to 25 ml. with water. This solution will be referred to subsequently as Solution A and was used for the calcium determination by the EDTA titration method and for the chloride determination by the Volhard method.

Other ash samples were dissolved in dilute nitric acid and made up to 100 ml. with water. This solution will be referred to subsequently as Solution B and was used for the sodium determinations by the flame spectrophotometric procedure.

Sodium by flame spectrophotometer (2).—A 50-ml. aliquot of Solution B was evaporated to dryness in a platinum dish on a steam bath. The residue was dissolved and made to 50 ml. with dilute hydrochloric acid. Following batch-wise treatment with an anion exchange resin to remove interfering anions, this solution was analyzed in the flame spectrophotometer for sodium.

Calcium by EDTA titration (3).—A 5-ml. aliquot of Solution A was transferred to a 3-inch casserole, the volume was made to 100 ml., the pH of the solution was adjusted to 12.5 with 10% potassium hydroxide, 0.2 g. of CalVer II* indicator (Hach Chemical Co., Ames, Iowa) was added, and the sample was titrated under strong artificial light with constant stirring until the color changed to a clear blue. The titrating solution was disodium dihydrogen ethylenediaminetetraacetate adjusted to pH 12.5 with potassium hydroxide and calibrated so that 1 ml. of solution was equivalent to 0.200 mg. of calcium ion.

Chloride analysis.—The chloride content of the hide samples was determined by the Volhard method (4). Five ml. of Solution A was shaken with 10 ml. of 0.1N silver nitrate, warmed on a steam bath, filtered, and washed. The filtrate was acidified with nitric acid, 2 ml. of 10% ferric ammonium sulfate was added, and the unreacted silver was titrated with 0.1N potassium thiocyanate to a brownish red tinge.

Lipid analysis.—A modification of Kissling's method (5) was used. The samples of hide were hydrolyzed for 4 hours by boiling in 15 ml. of concentrated hydrochloric acid plus 100 ml. of distilled water. This mixture was cooled, 100 ml. of Skellysolve B (a petroleum ether with a boiling range of 63°–70°C.) was added, and the mixture was shaken vigorously for 30 minutes. After settling, a 40-ml. aliquot of the Skellysolve layer was removed and evaporated to dryness, and the weight of the residue was taken as the amount of lipid in the aliquot of the sample.

RESULTS AND DISCUSSION

The individual diagrams of the location and size of tight hair spots for the 17 commercially limed hides that had tight hair spots were combined to produce

*Mention of specific brands or firm names in this paper does not imply their endorsement by the Department of Agriculture over others of a similar nature not mentioned.

Fig. 1. The numerical figures represent the number of hides which showed tight hair at the particular location. There were 8 hides showing tight hair spots on the shoulder, 12 showing spots along the butt end of the hide, and only 1 hide with a large tight hair spot in the center portion. It is obvious from the way the outlines of the tight hair spots overlap that several areas are more prone to develop tight hair spots than others. One of these is on the shoulder just to the right of the backbone, while 3 other such areas are at the rear of the hide: one slightly to the left of the backbone, one on the right side halfway between the backbone and the shank, and one on the left side just above the shank.

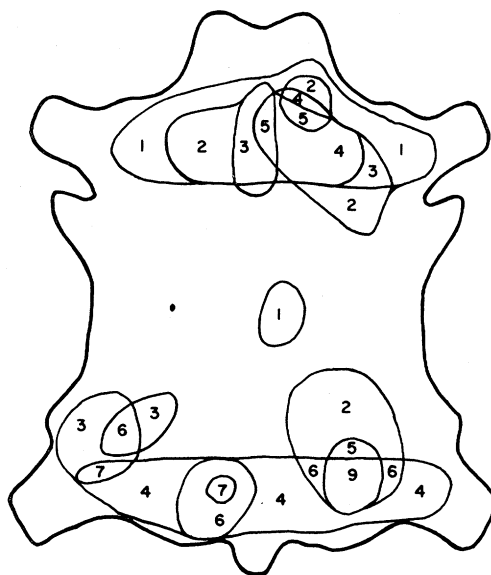


FIGURE 1.—Location and size of tight hair spots appearing on 17 commercially limed hides.

The data obtained from three samples cut from these commercial hides and three samples prepared in the laboratory are given in Table I. Sample AH is from the left-side butt area of a commercially limed hide. Its hair was still very tight. The corresponding control sample, AC, was taken from the un haired portion of the same hide adjacent to the tight hair spot. Sample BH is from the right-side butt area of a commercially limed hide. Its hair was moderately tight. The corresponding control area from the same hide is BC. Sample CH is from the backbone-butt area of a commercially limed hide. Its hair was moderately tight. The corresponding control area from the same hide is CC. Sample DH is from the neck area of a hide limed in the laboratory to try to reproduce the

conditions found in the commercially limed samples. Its hair was difficult to remove. The corresponding control sample from the same hide is DC. Sample EL is from a hide fully limed in the laboratory. Sample FS is from the salted hide used to prepare Sample EL.

TABLE I
ANALYSIS OF TIGHT HAIR SPOTS

Sample*	Calcium %	Chloride %	Sodium %	Water %	Ash %	Lipid %
AH	0.74	0.29	0.41	67	2.1	2.3
AC	1.16	0.13	0.25	69	2.2	1.8
BH	1.12	0.44	0.61	71	2.9	2.3
BC	1.18	0.24	0.34	69	2.2	2.2
CH	0.95	0.36		71	3.1	5.7
CC	1.10	0.35		74	2.9	4.1
DH	0.08	2.81		53	5.5	19.3
DC	0.56	0.83		65	3.6	15.2
EL	0.61	0.32		70	1.8	6.8
FS	0.14	2.69		62	5.0	3.8

*The second letter designates: H, tight hair spot; C, unhaired area; L, fully limed hide; S, salted hide after 1-day soak.

A comparison of the calcium contents of the test samples shows that the tight hair spots contained less calcium than the corresponding unhaired areas from the same hide. It must be remembered here that some time is required for lime to react with the epidermis to loosen the hair. In this study we are unable to show how long the lime has been at its final concentration in the unhaired spot. But the lower lime values for the tight hair spots indicate that it is taking a longer time for the lime to penetrate into them. The difference in calcium content is greatest in Samples A and D where the hair was still quite tight.

The sodium and chloride ion contents are higher in the tight hair spots than in the control samples. The values for sodium are not stoichiometric with those for chloride because of the sodium sulfide present in the lime solution. However, the higher concentration of both chloride ion and sodium in the tight hair spot above the level in the completely unhaired area indicates that there is more salt (sodium chloride) remaining in the tight hair spot. The higher value for chloride and lower value for calcium in Sample CC compared with that in Samples AC and BC indicate that the interchange of solution for Sample CC has not yet reached its final equilibrium value. Therefore, it appears that Sample CC has just barely reached the condition for satisfactory unhairing, while Sample CH has not quite reached it.

These comparisons indicate that the curing salt is not diffusing out of the tight hair spots and that the lime is not penetrating into them. This condition was duplicated in the laboratory by allowing a hide to remain in the lime until it would partially unhair. The results are shown under Samples DH, DC, EL, and FS. The original salted hide, FS, had a high value for chloride which also occurred in the tight hair spot, DH. The salted hide, FS, was soaked overnight prior to analysis. Sample D was limed following the overnight soak, yet the tight hair spot, DH, appears to contain more salt than the salted hide control, FS. The fully limed sample, EL, had a much higher calcium value and a lower chloride ion value which were almost duplicated in Sample DC, which was the control sample from the hair-free area adjacent to the tight hair sample, DH. Here again, we see that the salt has not diffused from, and the lime has not penetrated into, the tight hair spot.

The values for ash indicate that in most cases the sum of the inorganic constituents is greater in the tight hair areas than in the unhaired areas. The ash content reflects the amount of salts present; however, variations in the hides do exist, and other salts such as sodium sulfide used in the processing do contribute to the total ash content.

The lipid data are the only observations which give an indication of a cause for the delayed penetration of lime into the tight hair spots. In each case, except perhaps Sample B, the tight hair spot contains more lipid material than the hair-free control spot. If one considers the natural degree of variation of the fats in hides, which may be as high as a two-fold difference in adjacent pieces, the differences noted here between the tight hair spots and the unhaired areas may not be statistically significant. However, Strandine *et al.* (6) have indicated that fat on the flesh side of a hide reduces the rate of diffusion of salt into the hide, and Highberger and Moore (7) have shown that areas of hides which are covered with flesh have greater fat contents than adjacent areas which are free of flesh. This may explain the origin of the abnormally high fat content found in the D samples, which were produced in the laboratory and were known to have had a large amount of flesh present in the cured state.

McLaughlin and Theis (8) have determined the horizontal distribution of fat in steerhides, and although they have not studied all of the areas that we have shown in Fig. 1 as tight hair prevalent areas, they have reported much higher fat values in the tail, kidney, and rear flank areas than in other areas of the hide. These are in the region we have found most susceptible to tight hair spots. Therefore, the possibility exists that fat deposits, either on the flesh surface or within the structure of the hide, may lead to the formation of tight hair spots.

SUMMARY OF RESULTS

The high content of sodium and chloride ions present in tight hair spots indicates that the preserving salt is not being soaked out of these areas of the hide.

The low content of calcium ions present in tight hair spots indicates that the lime solution is slow in penetrating into the tight hair spots.

The slightly higher content of fatty materials in the tight hair spots over that in adjacent unhaired areas leads to the hypothesis that the fat is involved in hindering the flow of solutions through the tight hair spots. This slows down the removal of the preserving salt and the penetration of the lime, thus delaying the unhairing action.

ACKNOWLEDGMENT

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DISCUSSION

WILLIAM T. RODDY (Tanners' Council Laboratory): This is an example of laboratory investigators studying a commercial problem which has been very bothersome to the tanner from time to time on certain lots of hides.

Perhaps in our present system of curing hides we can all say that we have this salt and lipid problem.

For instance, if the hides are not fleshed and demanured when they go into a raceway system, the fatty flesh and manure will prevent the brine from going

into the hides. I think on the basis of the tanners' experience and what I have seen in the tannery that the problem of tight hair spots very rarely occurs on brine-cured, fleshed, and demanured hides.

It is shown that there is less moisture in these tight hair spots, which indicates that the hide hasn't been properly soaked back. There is certainly less lime in these tight hair spots on the basis of the tests that are given. It is mentioned, of course, that statistically perhaps it is not going to show a great difference, but on the other hand, this is the trend.

I would like to ask Miss Gruber and her coworkers if these figures which she has shown would not be more meaningful if they were based only on the epidermal area rather than on the total thickness, which I think was done in this particular case.

MISS GRUBER: Was the analysis done on the total thickness of the hide instead of the epidermal area? It was done on the total thickness.

MR. RODDY: It is definitely indicated then that the figures would probably spread much further apart if only the epidermal area had been used, because it is indicated, for instance, that the salt perhaps did not get into the hide until much later in the curing operation and then in turn by capillary action perhaps built up in that area to a greater extent. Then also in turn, any type of breakdown of the hide would prevent this salt from coming back out. Lipids are always a barrier in any type of aqueous system, so it would be indicated that if only the epidermal area were used instead of full thickness, better comparison values would be obtained. It was mentioned that the hides were commercially unhaired. Was this a pit or a paddle type of liming?

DR. EDWARD F. MELLON (Eastern Regional Research Laboratory, United States Department of Agriculture): These hides were limed with a pit liming process. The reason we happened to have the samples is the tannery was getting a larger proportion of tight hair spots than normal. We happened to be visiting the tannery at the time and had the opportunity to get these spots and study them.

I think we have to consider two things. The tannery was having trouble. This wasn't the normal operation. We had to take the samples as we found them. We didn't have the chance of carrying on any special production for the samples. Therefore, in interpreting the figures, we have to remember that these tight hair spots had a wide variation of degree of completion. Some of them were almost ready to unhair, and some of them still had a long way to go.

We are at the present time trying to develop techniques for separating the fats into various components. I don't think that all of the fats are involved in the situation. It probably is only one component, and perhaps it is related to what Mrs. Tancous will be talking about in her paper.

It is very possible that something is happening to the fatty component in these hides due to poor storage conditions or something of that nature.

We have studies going at the present time to determine the distribution of various components of fat in the hide. After this study is completed, we may be able to restudy the tight hair spots and the role of fats in making them.

I. LEO RIESE (Allied Kid Company): One of the tables seemed contradictory to me — the table headed "Lipid Content." There it indicated that the particular hide that was impossible to unhair had a lower lipid content, which seems to be contradictory to what you were saying. I was wondering if that is a typographical error or just what it was.

MR. RODDY: The one that was impossible to unhair is the salted hide. It had not sufficient soaking or liming. It was the control piece. That is the reason it was impossible.

CHAIRMAN STUBBINGS: I realize the problem has been studied on a specific complaint and set of tannery hides, but I am wondering if the caustic content, that is the caustic alkali content versus the lime alkali content, would have a bearing on the penetration in these heavy fatty hides. Hides with a great amount of fat on the adipose tissue seemed to indicate in most of the studies of unhairing systems that caustic alkali penetrates through the fatty deposits more readily than lime does. I wonder whether those studies are part of this particular program.

Also at the same time you might as well answer a question about the effect of temperature on this same phenomenon.

DR. MELLON: We did not have the techniques readily available at the time for determining the difference between our lime and sodium alkali content of the hides. We had the hides and we had to process them as fast as we could in order to assure that nothing would change in the meantime.

Therefore, we had to use the techniques that we already had worked out. Possibly in any future studies we will look into this matter.

We also do not have any effects of temperature. I think all of these were done more or less at room temperature. The liming in the commercial study, in the commercial hides, was done in the pit. I guess they started out with tap water, which was down somewhere in the sixties, and I guess it was a big volume. It didn't have much chance of warming up during the 24 to 48 hours that the hides were in the lime.

MR. RODDY: There is one question which I think is in everyone's mind. That is, what does the tanner do when he has the tight hair spots and a schedule to

meet? If he throws it back in the lime, where is the next unhairing spot to occur in the tannery? This, of course, is naturally a problem not only on tight hair spots but also on fine hairs.

I would like to ask Dr. Mellon if he feels that the same type of mechanism on tight hair spots as we have on fine hair exists, or if the fine hair is perhaps a problem where the hair would probably come out if the hide were left in the lime liquor for just a shorter period of time in contradistinction to putting the tight hair spots back into the lime liquor for another day or so.

DR. MELLON: I think the problem with the tight hair spots may be twofold. The hair is so much finer than the coarse hair that it is possibly difficult for the unhairing machine to grab hold of it and pull it out. Also the hair follicle may be smaller in diameter. Therefore, it may be harder for the unhairing solution to penetrate down along the hair shaft.

I think we have to remember that in unhairing we do not get unhairing immediately as soon as these solutions penetrate into the hide. The solution has to penetrate, and after it has reached the place where it is going to act, it takes a little time for it to act. I don't believe anybody has determined how long the lime actually has to be there before the hair becomes loosened.

DR. FRANK W. PANEPINTO (William Amer Company): Have you found whether this effect can also be produced by concentrated solutions either of salts or concentrated caustic? I found certain cases where the accidental spillage, for instance, of concentrated caustic would cause a change.

DR. MELLON: We haven't determined anything like that, except we do have to be careful. I remember one time when they were using calcium chloride solution in the lab and accidentally spilled some on a piece of hide. This reduced the shrinkage temperature, so that the material shrank at room temperature. We had to start over with a new piece of hide.

Salt effects do make a tremendous difference. In these experiments we should consider that the salt was not much different than normal practice, because the hide, as far as the hide processor was concerned, had the standard treatment. I presume they were all pack-cured hides, and the salt concentration would be as uniform as in any salt-packed hides.

DR. PANEPINTO: How about concentrated caustic?

DR. MELLON: I couldn't answer that. It seems to me that concentrated caustic probably would take the hair off a lot faster than lime. I think it would also damage the hide to some extent if left on too long.

MRS. JEAN J. TANCOS (Tanners Council Laboratory): The fact that these spots are in definite patterns in the shoulder and bend area would rule out any spillage because that could be on any part of the hide, and these are in a definite pattern.

DR. MELLON: I agree with that as far as these hides are concerned, but you could also have other effects than what we have detected here which would cause tight hair spots and loose hair spots on hides at other times.

PRESSLEY DOWNES (Rohm & Haas): As a result of this study has the tannery where these tight hair spots have been a problem effected any changes for the better? Has this paper helped in that regard?

DR. MELLON: They wouldn't tell me how the leather was turning out, but they did have a few problems. In a few places they had to shave a little heavier. They obviously had tried sanding off some of the spots. Usually they just threw them back in the lime and then let them go for another day. Then they unhaired beautifully. It is actually a time phenomenon that we are working with. The reason that we made this study was that if we could in any way reduce the length of time that it takes to remove the hair from the spots where the hair is most persistent, then we could shorten the time of unhairing considerably.

If you put a hide into a lime vat, after one day you find some areas of the hide where you can almost remove the hair; if you leave it in two days, then you remove the hair from most of the hide. If we could make all of the hide unhair as easily as the most easily unhairable part at the present time, we could possibly shorten the unhairing process by maybe a day.

S. S. SARYAN (Allied Kid Company): We recently received a shipment of goatskins from India. After the normal liming operation and unhairing operation, we were unable to remove all the hair. We left many spots on the skins. I would like to know if anyone else has observed this and what we might do to eliminate it.

DR. MELLON: I don't know of anything. We haven't worked with goatskins.

MR. RODDY: Were these denatured goatskins or standard salt-cured goatskins?

MR. SARYAN: They were salt-cured goatskins which came in wooden barrels.

MR. RODDY: You still had tight hair spots. I hope someone in the group here can help the individual out who asked the question.

DR. THOMAS THORSTENSEN (Thorstensen Laboratory): With regard to the goatskins, I think that certainly Allied Kid knows better than anyone that there is no such thing as a standard cured goatskin in India.

The salt conditions depend a great deal upon the area, whether the salt comes from the solar evaporation in the sea or from the salt lakes of the inland. Sometimes they are mud-cured, and they are dried. I think the salt is the main condition.

The curing conditions are unbelievably primitive, and inconsistency I would expect to be the normal rather than the exception.

EDWIN J. KAINE (John J. Riley Company): I think we have been talking about the same hair type process, where we have the mechanical removal of hair. Obvious results can be shown by the lack or inability to have it removed.

In the process where you destroy the hair, we still have these same conditions that exist because of the nature of the way the hair is removed. All that would be left in the hide would be the follicular part of the shaft. What could be done about this? The leather would be put almost all the way through the buffing room before you possibly see the damages.

DR. MELLON: So far our experimentation has been at the stage of trying to find out what is happening in these tight hair spots. We hope eventually to get enough information so that we can propose a solution. Whether the proposed solution will be economical or not is a different question. I think it will take some additional study to find the answer to this question.

MR. KAINE: One piece of evidence we have found in our tannery that comes to light here is that there is a lot of inconsistency in the amount of hair root that is left.

We use a destroyed hair process. It isn't until buffing that we see the results of the damage. Where shoulder buffing is done there is an overlapping of cuts. It is a pretty horrible looking area in the shoulder because of the many hair roots which are left. This we hadn't been able to see down in the liming department.

DR. MELLON: I think probably this is very characteristic of the hair destroying process, that the hair that is exposed on the surface is quite available to all the solution, but that which is down in the hide below the surface of the skin has to be reached by an unhairing solution. It is probably the last part of the hair to disappear.

Probably the easiest solution would be to allow the unhairing to occur for a little longer time. This may not be economical in the tannery.

MR. RODDY: Thank you very much for the discussion period. I am sure that Miss Gruber, since this is her first time to address the ALCA, has been happy with this. I would like to say that in the history of ALCA this is the first time that a lady presented the first paper at our technical sessions.

HERBERT A. TETREULT (Rohm & Haas Company): The organization for years has been requesting the cooperation of tanners in the presentation of papers. I think this is a classic example, and I hope that the tanners present will take note of it.

Here is a practical problem that was pretty well elucidated through a non-sophisticated method of analysis available to all of us. The type of discussion that was engendered by the paper, I think, showed the interest of the tanners in the problem.

It seems to me this is the sort of thing we would expect and hope in the future to get from our tanner members.